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MARTENSITIC PHASE TRANSITIONS IN NANOCRYSTALLINE MATERIALS

Final Technical Report

by

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May 1989

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1. Abstract

The martensitic transformation in Fe-Ni alloys (Ni content between 31 wt% and 36 wt%) was studied by means of X-ray diffraction and transmission electron microscopy in nanocrystalline specimens (polycrystals with a crystal size of 4 nm) as well as in a loose powder of 4 nm sized, isolated Fe-Ni crystals with the same chemical compositions as the nanocrystalline materials. The isolated crystals were embedded in pure paraffin. The results obtained indicate that a martensitic transformation does not occur in the nanocrystalline material because the formation of a martensitic nuclei is inhibited due to the small size of the crystals. The inhibition of a martensitic phase transition may be of technological interest for the generation of improved superconducting, ferromagnetic and ferroelectric materials.

2. Introduction

Martensitic phase transitions in bulk materials involve the following two processes: the shear of the parent crystal lattice (occasionally also called matrix or austenite phase) into the martensitic structure and the lattice invariant transformation. The latter transformation is required to make the martensitically transformed region compatible in shape with the surrounding (untransformed) matrix. The lattice invariant transformation may occur by shear and/or twinning (for a review cf. ref. 1).

Atomistically, both processes involve the motion of a two-dimensional array of dislocations through the crystal lattice of the parent phase. This array of dislocations forms the interface between the martensitic lattice and the surrounding parent lattice. Obviously, if the diameter of the crystals undergoing a martensitic transformation is reduced to a size comparable to the spacing of the dislocations in the dislocation ar-

ray of the martensite/matrix interface, the martensitic transformation in such small crystals may be modified in comparison to a bulk material.

In order to investigate this size effect, several studies of martensitic transformations in small crystals have been carried out in the past. Small Fe crystals (diameters between 15 nm and 30 nm) precipitated coherently in a Cu matrix did not exhibit any martensitic transformation (2),(3) during cooling to liquid He temperature although the M_s temperature of bulk Fe crystals with the same chemical composition was about 600°C. Plastic deformation of these crystals induced a martensitic transformation in crystals larger than 20nm. This result was interpreted in terms of the following nucleation model. Initially the small crystals are dislocation free so that the nucleation of the dislocation array required for the transformation is inhibited. Plastic deformation introduces dislocations into the small Fe crystals and may thus permit nucleation. If the crystal diameter becomes equal or less than the critical nucleation size, the transformation is prevented.

This criteria was assumed to apply to crystals below 20 nm size because no transformation was observed even after plastic deformation. In fact, this hypothesis agrees with the dislocation model of the martensitic nucleation (4). In order to investigate the effect of the surrounding Cu-matrix on the nucleation of martensite in small single crystals, Easterling and Swann (5) extracted the small Fe and Fe-Ni precipitates from the Cu matrix by an electrochemical method. Fe particles with low or zero Ni content transformed to single crystal twinned martensite when extracted. With increasing Ni content the volume fraction of the martensitically transformed material was progressively reduced. In small Fe-Ni crystals which transformed partially at ambient temperatures, no further transformation occurred upon cooling to liquid N_2 temperature, due to difficulties in nucleating the dislocations required for the relaxation of the stresses associated with the martensitic

transition.

A similar tendency was noted in a fine grained polycrystalline Fe-Ni alloy (6) (7). A reduction of the crystal size decreased the M_s temperature due to the lack of lattice defects suitable to provide nucleation sites for martensite nucleation. This conclusion was recently confirmed (8) by studying the nucleation of martensite in isolated dislocation free Fe-Ni single crystals, the free surface of which was prevented to act as a nucleation site by an enhanced Ni-content of the surface region. The Ni-enhanced surface region was generated by diffusing Ni from the free surface into the crystals. Hence, on the basis of these observations, it seems possible to inhibit the martensitic transformation of solids*) by reducing the crystal size of a polycrystalline material to a few nanometers.

The inhibition of the martensitic transformation may be technologically desirable; for example, if the properties of the parent phase are superior to the ones of the martensite. This is the case in superconductors of the A15 or B1 type (e.g. Nb_3Sn ; V_3Si). The enhancement of T_c by increasing the solute content is limited by a martensitic transformation at higher Sn or Si concentrations (9),(10). If the transformation could be prevented, T_c could be raised further by increasing the alloy concentration. Similar arguments apply to some ferromagnetic and ferroelectric materials.

It was the purpose of this study to investigate the question whether or not martensitic transformations may be prevented by reducing the crystal size of a polycrystal to a few nanometers. The model systems chosen were Fe-Ni alloys with an average crystal size of about 4 nm. Fe-Ni alloys were chosen because they offer two advantages. The martensitic nucleation has been

*) This may not apply to martensitic transformations nucleating by a soft mode mechanism. In the case of Fe-Ni alloys the volume change during the $fcc \rightleftharpoons bcc$ transformation is about 4% and thus prevents a soft mode mechanism (1).

studied most extensively in these alloys and it is known to occur by a dislocation mechanism (4) (8). By varying the Ni-content, the M_s temperature may be tuned to an experimentally convenient value.

3. Experimental

Fe-Ni polycrystals with a crystal size of about 4nm (called nanocrystalline Fe-Ni-alloys) were generated by the inert gas condensation method (11). Fe-Ni alloys with a Ni content varying between 30 wt% and 50 wt% Ni were obtained by melting Fe(99.9%) and Ni(99.8%) in vacuum (10^{-6} Pa). Small quantities (~1g) of these alloys were evaporated in a UHV evaporator filled with 6N-He (1kPa He-pressure) (Fig. 1). The evaporated Fe-Ni-alloy condensed in the He in the form of 4 nm sized crystals. These crystals accumulated at the surface of a cold finger held at -20 °C. After restoring UHV conditions, the small Fe-Ni crystals were scraped off and either consolidated in a piston and anvil device at about 2GPa into a nanocrystalline Fe-Ni alloy or were immersed in the form of a suspension of predominantly isolated Fe-Ni crystals in molten pure paraffin at 50 °C. Paraffin was chosen to prevent oxidation when the specimens were exposed to air.

The chemical compositions of the nanocrystalline Fe-Ni alloys were analysed by an electron microprobe (Jeol JXA-840A) utilizing pure-element Fe, Ni standards. Depending on the evaporation conditions, the Ni content of the nanocrystalline samples varied between 18 wt% and 42 wt%. The specimens contained between 0.2 wt% and 0.7 wt% W. The Ni content may deviate by about $\pm 2\%$ from the average Ni concentration within the specimen. The accuracy of the chemical analysis was $< 1\%$.

The specimen morphology and crystal size was investigated by transmission electron microscopy of thin foils (Jeol 200 CX) prepared by ion beam polishing. The structure was studied by

Mössbauer spectroscopy and X-ray diffraction at 20°C (Siemens D500, Cu K α secondary monochromator, 40 kV, 30 mA, 0.02° resolution, step width 0.05°, counts per step in the peak vicinity 5000-10000) and at -183°C in a low temperature diffractometer (Physics Department of the University of Munich, MoK α primary monochromator, 50kV, 32 mA, 0.17° resolution, step width 0.15°, counts per step in the peak vicinity about 4000).

In order to see whether or not the martensitic phase transformation is suppressed in nanocrystalline materials, nanocrystalline Fe-Ni alloys consisting of a mixture of austenite and martensite were utilized. By means of X-ray diffraction, the relative fractions of austenite and martensite were measured in the following temperature cycle: First measurement at 20 °C (as prepared state), second measurement performed at -183 °C and a third measurement was carried out after re-heating to 20°C. A complementary measurement was performed after the specimen was cooled again from 20 °C to -269°C for 2 minutes and then reheated to 20°C. The same measurements were carried out with the loose Fe-Ni crystals embedded in paraffin. Mössbauer spectra of the same specimens were recorded at 20 °C and -269 °C.

4. Results

Nanocrystalline Fe-Ni alloys (4 nm crystal size) with less than 31 wt% Ni were found to consist of 100 % martensite, alloys with more than 36 wt% Ni had a fcc structure (austenite). Hence the present studies focused on Fe-Ni alloys between 31 wt% and 36 wt% Ni. Fig.2 shows the microprobe analysis of a nanocrystalline Fe-Ni alloy containing about 34 wt% Ni. In addition to Fe and Ni, a small peak corresponding to W may be noticed.

Fig.3 shows a dark-field electron micrograph (taken with a fcc-200 reflection) and the corresponding electron diffraction pattern of a nanocrystalline Fe-Ni (34 wt%) specimen. Diffraction rings from austenite (fcc phase) and martensite (bcc phase) are present.

In Figs. 4a,b, the X-ray diffraction data of the same nanocrystalline Fe-34wt% Ni specimen taken at 20°C and -183°C are compared. The two curves do not show any significant deviation. This applied to all specimens consisting of an austenite and martensite mixture, irrespective of the relative fraction of both phases. Also, specimens consisting of 100% austenite did not show any martensite formation upon cooling. Specimens cooled from 20°C to -269°C followed by a subsequent reheating to 20°C did also not exhibit any change in the X-ray diffraction curve recorded at 20°C before and after cooling.

A similar behaviour was noticed for the suspension of small, isolated Fe-Ni crystals embedded in paraffin. Figs 5a,b compare the diffraction curves of the same specimen at 20°C and -183°C. In Fig. 6, the diffraction curves before and after cooling to -269°C of the same specimen containing martensite and austenite are shown. Again, in all three figures, there is little evidence for any variation of the relative volume fractions of both phases upon cooling.

Mössbauer spectroscopic studies were performed in order to measure the relative volume fraction of the austenitic and martensitic phase in Fe-Ni alloys at 20°C and -269°C. The resolution of the spectra obtained turned out not to be sufficient to monitor a variation of the relative volume fractions of both phases. Structural studies by Mössbauer spectroscopy of isolated small Fe-Ni crystals are hampered at elevated temperatures by the superparamagnetism of these crystals.

5. Discussion

The experimental observations (Figs. 4a,b,5a,b and 6) reported indicate that Fe-Ni alloys consisting of austenite and martensite or of pure austenite do not exhibit any martensitic transformation upon cooling to -269°C. This result agrees with previous observations on the martensitic transformations in polycrystals with small crystal sizes. Two reasons are conceivable for the inhibition of martensitic phase transformations in nanocrystalline Fe-Ni alloys. The nucleation may be prevented

e.g. due to a lack of suitable nucleation sites^{*)} and/or due to the small size (4nm) of the crystals which may be comparable to the dimension of a martensitic nuclei. Secondly the small crystal size may prevent the growth of martensitic nuclei due to internal stresses. The lattice invariant shear/twinning generates ledges of atomic size at the surface (grain boundary) of a transformed crystal. These ledges can be accommodated elastically if the crystal size is large in comparison to the height of the ledges. In nanocrystalline materials this is not so. Hence, the elastic strain associated with the lattice invariant shear/twinning is large and may prevent the transformation. Clearly, in small isolated Fe-Ni crystals the latter effect would be irrelevant. Hence, if the martensite formation in nanocrystalline materials is nucleation controlled, consolidated nanocrystalline Fe-Ni alloys as well as the loose powder of isolated small Fe-Ni crystals of the same crystal size and chemical composition should not exhibit a martensitic transformation. If the transformation is growth controlled, the powder should transform upon cooling but not the consolidated material. As both, the powder and the nanocrystalline alloys did not exhibit martensitic phase transformations upon cooling, one is led to conclude that the small crystal size prevents the formation of martensitic nuclei.

^{*)} HREM indicates that the majority (or all) crystals of a nanocrystalline material are free of lattice dislocations.

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7. Figure Captions

Fig. 1 Schematic drawing of the arrangement used to generate nanocrystalline materials. Cf = cold finger, E = evaporator, C = compaction device.

Fig. 2 Electron microprobe analysis of a nanocrystalline Fe-34wt%Ni specimen. The elements indicated by the maxima are Fe, Ni and W.

Fig. 3 Dark-field electron micrograph - $(200)_{fcc}$ reflection - of a nanocrystalline Fe-34wt%Ni specimen and corresponding electron diffraction pattern of the same specimen.

Figs. 4a,b X-ray diffraction diagram of a nanocrystalline Fe-34wt%Ni specimen recorded at 20°C (Fig. 4a) and -183°C (Fig. 4b) in reflection geometry. The specimen was mounted on a Si single crystal which enhances the intensity in the vicinity of two theta 30°. The diffraction diagrams shown in Figs. 4 and 5 were recorded by using MoK α .

Figs. 5a,b Same diagram as in Figs. 4a,b for the suspension of small Fe-34wt%Ni crystals in paraffin. Fig. 5a was recorded at 20°C and Fig. 5b at -183°C. the rapid reductions of intensity below two theta 18° is due to the aperture of the low temperature X-ray stage.

Fig. 6 Same specimen as in Figs. 5a,b after cooling to -269°C and re-heating to 20°C. The diagram was recorded using CuK α . To avoid coincidence of both curves, the upper one has been shifted vertically by a constant amount (about 25 cps).

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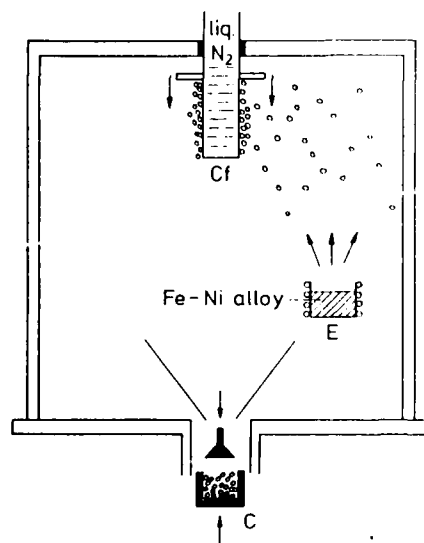


Fig. 1

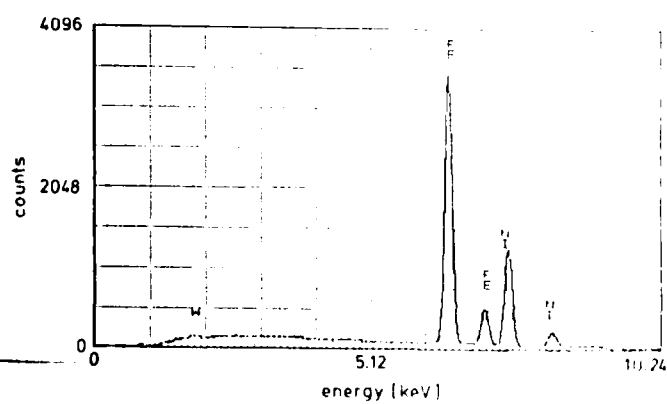


Fig. 2



Fig. 3

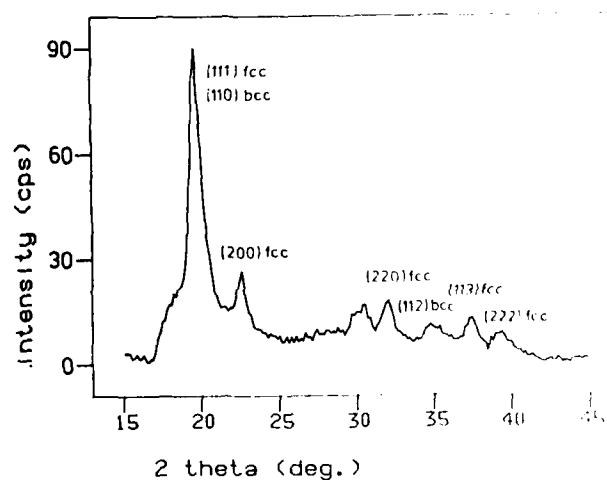


Fig. 4a

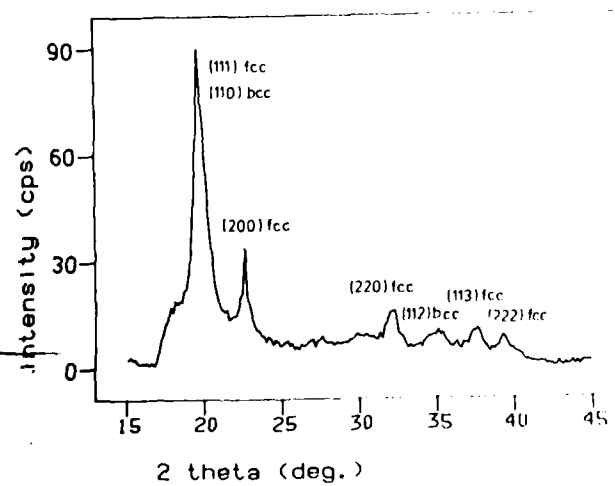


Fig. 4b

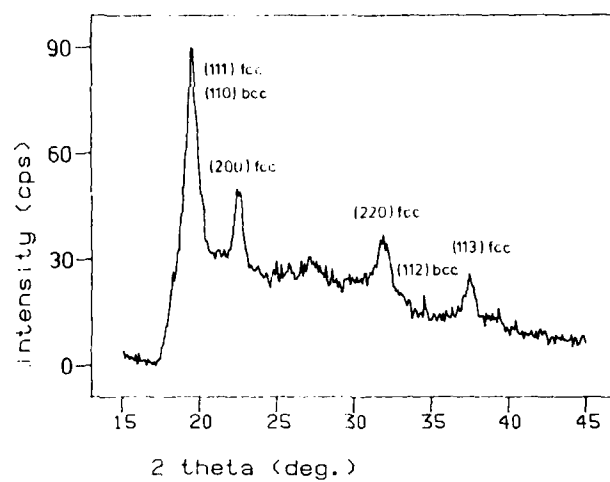


Fig. 5a

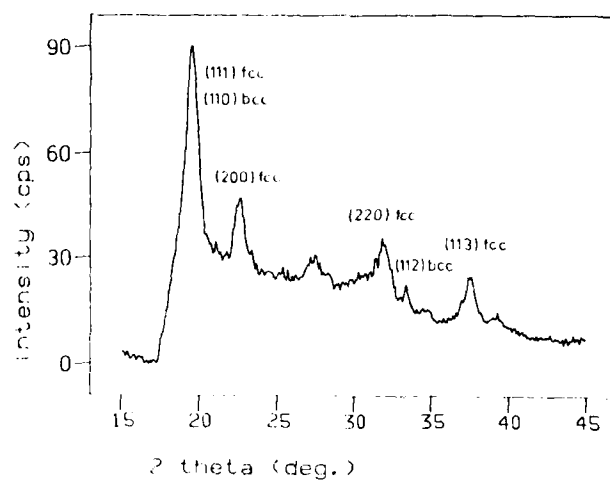


Fig. 5b

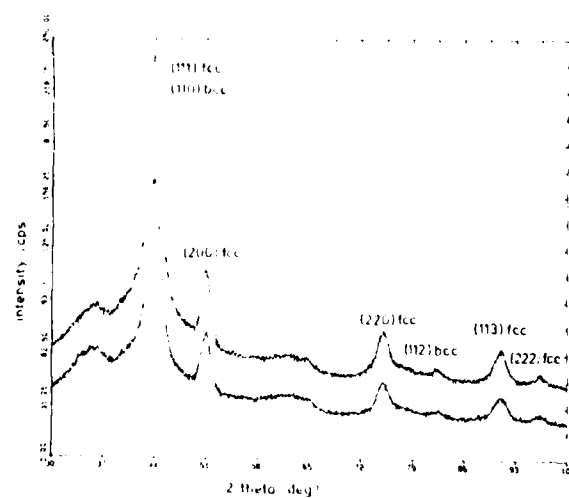


Fig. 6